

Docket No.: H0610.0348/P348
(PATENT)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of:
Thomas Rostrup-Nielsen, et al.

Application No.: Not Yet Assigned

Filed: Concurrently Herewith

Art Unit: N/A

For: PROCESS AND APPARATUS FOR THE
PREPARATION OF SYNTHESIS GAS

Examiner: Not Yet Assigned

CLAIM FOR PRIORITY AND SUBMISSION OF DOCUMENTS

MS Patent Application
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

Applicant hereby claims priority under 35 U.S.C. 119 based on the following
prior foreign application filed in the following foreign country on the date indicated:

<u>Country</u>	<u>Application No.</u>	<u>Date</u>
Denmark	PA 2002 01432	September 26, 2002

Application No.: Not Yet Assigned

Docket No.: H0610.0348/P348

In support of this claim, a certified copy of the said original foreign application is filed herewith.

Dated: September 23, 2003

Respectfully submitted,

By 

Stephen A. Soffen

Registration No.: 31,063

DICKSTEIN SHAPIRO MORIN &
OSHINSKY LLP

2101 L Street NW

Washington, DC 20037-1526

(202) 785-9700

Attorney for Applicant



Kongeriget Danmark

Patent application No.: PA 2002 01432

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Applicant: Haldor Topsøe A/S
(Name and address) Nymøllevej 55
DK-2800 Kgs. Lyngby
Denmark

Title: Fremgangsmåde og apparat til fremstilling af syntesegas


IPC: C01B 3/38; B01J 8/06

This is to certify that the attached documents are exact copies of the above mentioned patent application as originally filed.



Patent- og Varemærkestyrelsen
Økonomi- og Erhvervsministeriet

13 August 2003


Ase Damm

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HALDOR TOPSØE A/S +45 45272999

NO. 0131 P. 4/25



HALDOR TOPSØE A/S

HYMØLLEVEJ 55 · P.O. BOX 215 · DK-2800 LYNGBY · DENMARK · CVR NO. 41853816 · VAT NO. DK 41853816
TELEPHONE: +45 4527 2000 · FAX: +45 4527 2999 · WWW.HALDORTOPSØE.COM

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Process and Apparatus for the Preparation of Synthesis

Gas

GB-280

Modtaget i VS

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The present invention relates to a process and an apparatus for the preparation of synthesis gas. The preparation process includes catalytic steam and/or carbon dioxide reforming of a hydrocarbon feedstock. In particular, the invention provides an improved process of the above type including the steps of heated steam reforming of a hydrocarbon steam mixture in contact with catalysed hardware having activity in steam reforming and subsequently reforming the partially reformed effluent in a fired steam reformer.

10

Partial steam reforming upstream of a fired steam reformer in the form of pre-reforming of a hydrocarbon feedstock in the preparation of synthesis gas is well known in the art. Pre-reforming is generally employed with hydrocarbon feed containing higher hydrocarbons or for increasing the capacity of existing reformer plants. Process gas of the hydrocarbon feedstock and steam and/or CO_2 is thereby introduced in a pre-reformer at temperatures of about 450°C to 550°C . By the steam reforming reactions proceeding in the pre-reformer, the temperature in the process gas usually decreases or increases slightly when carrying out the pre-reforming process depending on the hydrocarbon feedstock as it is an adiabatic operation.

25 In industrial synthesis gas preparation plants, the pre-reformed process gas to which CO_2 may be added is subsequently reheated to the desired inlet temperature to the fired steam reformer by heat exchange with hot flue gas from the fired steam reformer. The usual inlet temperature into an industrial reformer is between 600°C and 700°C .

Introducing a flue gas heated steam reforming step in between the pre-reformer and the fired steam reformer will result in an increased utilisation of the flue gas heat content, while it is possible to keep the inlet temperature
5 between 600°C and 700°C. However, the application of the process of the invention is not limited to this temperature interval.

10 Increased utilisation of the heat content in the flue gas for reforming is desirable as it reduces the size of the fired reformer and reduces the waste heat used for steam generating thereby limiting the steam export, which may be undesirable.

15 Improved utilisation of heat in the hot flue gas from the fired steam reformer is disclosed in EP patent application No. 855,366. This publication describes a process whereby process gas to the steam reformer is partly reformed in a pre-heater coil provided with a thin film of steam reform-
20 ing catalyst on the wall of the coil. A high amount of valuable heat in the flue gas is then transferred to and absorbed by the process gas through endothermic steam reforming reactions proceeding on the wall-coated catalyst. The coil dimension and amount of catalyst is thereby ad-
25 justed to increase the exit temperature in the partially reformed process gas from the catalysed pre-heater coil to the required temperature at inlet to the fired steam reformer.

30 The main disadvantage of this process is decreasing catalyst activity at long time operation of the catalysed pre-heater coil. This results in a coil exit temperature above

the maximum allowable gas temperature at the inlet of the fired steam reformer. The increased coil exit temperature is due to decreased heat absorption at diminished steam reforming in the gas. The catalyst has then to be reactivated or replaced with fresh catalyst on the coil wall. Replacement of catalyst in the pre-heater coil is a difficult and expensive operation when demounting the coil from the flue gas channel.

10 The objective disclosed in EP patent application No. 1,069,070 is to improve long term operability of a steam reforming process of the above type by compensating a decreasing catalyst activity in the catalysed pre-heater coil by means of an additional catalyst unit being easy to replace.

This publication discloses a process for the catalytic steam reforming of a hydrocarbon feedstock, and includes steam reforming a hydrocarbon steam mixture in contact with a first steam reforming catalyst being arranged in catalysed pre-heater coil in a flue gas channel from a fired steam reformer. Contacting partially reformed effluent from the catalysed pre-heater coil with a second steam reforming catalyst in a fired steam reformer follows this step. The process includes the further step of contacting the partially reformed effluent with an intermediate reforming unit arranged between the outlet of the catalysed pre-heater coil in the flue gas channel and the inlet of the fired steam reformer.

30 Loss of activity in the catalysed pre-heater coil unit during long time operation is compensated by steam reforming

reactions in partially reformed effluent within the intermediate reforming unit. The intermediate unit is operated at substantially adiabatic conditions and compensates decreasing steam reforming activity of the steam reforming catalyst (or catalysed hardware) in the catalysed pre-heater coil and the resulting temperature increase in the effluent from the catalysed pre-heater coil.

Besides providing the required temperature adjustment of the process gas below the maximum inlet temperature into the fired steam reformer at long term operation, a further advantage of the intermediate reformer unit is the siting of the unit outside the flue gas channel. To compensate decreasing activity in the catalysed pre-heater coil as described above, it will be necessary to replace or reactivate spent catalyst upstream the fired steam reformer. As mentioned earlier replacement of spent catalyst in a unit within the flue gas channel is time consuming and expensive to handle.

By arranging an intermediate catalyst unit outside the flue gas channel, spent catalyst is then replaced in the intermediate reformer unit and the replacement operation simplified considerably.

The processes described in EP 855,366 and EP 1,069,070 both have the disadvantage of difficult replacement of the catalyst in the catalysed pre-heater coil in the flue gas channel.

US parent No. 3,743,488 describes a process in which the hydrocarbon steam mixture is repeatedly heated in a flue

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gas steam and reacted in adiabatic reactors external to the flue gas stream, with steam reforming catalyst pellets. This concept offers easier access for change of the catalyst in the external reactors. However, the use of many
5 adiabatic reactor vessels is overall an expensive solution.

The process described in US patent No. 4,959,079 is designed with the purpose of improved utilisation of heat in the hot flue gas from the fired steam reformer. In the process the process gas to the steam reformer is partly re-
10 formed in a pre-heated section of the reformer tube that extends from the radiant chamber. Valuable heat in the flue gas is then transferred to and absorbed by the process gas through endothermic steam reforming reactions. However,
15 heat exchange in counter current flow between the flue gas and the reforming tube is poor. Introducing fins on the reforming tube increases the heat transfer. Despite this the amount of heat transfer possible is relatively limited if the reformer tube length is to be kept at a reasonable
20 length.

The process of the invention solves the problems occurring with the prior art by providing an improved process including the step of steam and/or CO₂ reforming a hydrocarbon
25 steam mixture in contact with a solid catalyst having activity in steam reforming. The solid catalyst, for instance catalysed hardware, is arranged in piping system of a flue gas heated coil system, constituting a steam reforming unit. Subsequently, the effluent from the steam reforming
30 unit is contacted with a steam reforming catalyst in a fired steam reformer. By locating some or all of the steam reforming catalyst of the steam reforming unit as catalysed

hardware in adiabatic zones of the piping system of the heated coil system outside the flue gas channel, easy catalyst replacement is achieved, while at the same time achieving improved utilisation of the heat content in the flue gas for steam reforming.

The invention therefore provides a process for the preparation of synthesis gas by catalytic steam and/or CO₂ reforming of a hydrocarbon feedstock comprising the following steps:

- a. heating the reaction mixture of hydrocarbon feedstock and steam and/or CO₂ in the flue gas containing waste heat section from the fired tubular reformer
- b. adiabatic reforming of the reaction mixture outside the waste heat section by contact with a solid reforming catalyst
- c. repeating steps a. and b. until the desired reaction mixture composition and temperature is reached
- e. feeding the reaction mixture to the fired tubular reformer and further reforming the mixture to the desired composition and temperature, wherein the adiabatic reforming of the reaction mixture is conducted in the process gas piping system in the flue gas-containing waste heat section, the piping system having adiabatic zones outside the heating section and containing solid reforming catalyst.

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The invention also concerns an apparatus for use in the above process comprising the following:

- a. an adiabatic pre-reformer for optional pre-reforming of a mixture of hydrocarbon feedstock and steam and/or CO₂
- b. a fired tubular reformer with a flue gas-containing waste heat section for heating of a mixture of hydrocarbon feedstock and steam and/or CO₂ or of the pre-reformed mixture
- c. a process gas heating coil integrated in the flue gas-containing waste heat section
- d. a steam reforming unit system outside the waste heat section

wherein the steam reforming unit system is integrated in the process gas piping system of the piping system of the heated coil system in the flue gas-containing waste heat section, the piping system having adiabatic zones outside the heating section and containing solid reforming catalyst.

The various embodiments of the invention allow for easy replacement of the catalysed structured elements, efficient heat transfer between the flue gas and the process gas, and an economically attractive design due to the high level of integration of functions.

The steam reforming unit system is integrated in the process gas piping system, and is located in the flue gas-containing waste heat section from the fired tubular reformer. The piping system can be structured in various ways. The reheat sections can consist of several parallel

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tubes connected to common feed and product headers. For instance, the process gas enters a heating coil through an inlet header, followed by collection in an outlet header placed outside the heating section. This outlet header is
5 connected to an inlet header for the next reheat coil section with a connecting element.

In the inventive process structured elements that are catalysed are placed in the normal process gas piping system.
10 The catalytic element can be placed in the header system connecting one heating coil to the next, e.g. in the headers themselves or in the transitional zone between the two headers. The inlet- and outlet headers and the transitional zone between the two headers form adiabatic zones.

15

In another embodiment of the invention, a first catalytic element can be placed in the outlet header and a second catalytic element placed in the inlet header to the following reheat section.

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In a further embodiment of the invention, the process consists of adiabatic steam reforming in a process gas piping system where the individual tubes are extended outside the heating zone. Each tube is then connected to the subsequent
25 tube by a U-tube or similar element outside the heating zone. The tube extensions outside the flue gas channel and the tube-connecting elements comprise adiabatic zones in which catalyst can be situated.

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Another embodiment of the invention consists of a process where the steam reforming additionally takes place in the process gas piping system in the reheating section inside

the waste heat section, the reheating section having for instance structured elements that may be separated by spacers. Cross corrugated elements can be used in this case in addition to the structured elements placed in the header system. Conventional catalytic pellets can also be used in the piping system in the reheating section.

The number of reheating steps followed by adiabatic reforming in the header sections containing catalytic elements can be varied in the process of the invention.

Various solid reforming catalysts can be incorporated into the piping system of the heater. Catalysed hardware in the form of a structured element with a catalytic layer is suitable for use in the process of the invention. Two types of structured elements are particularly suitable for the inventive process - the straight-channelled elements and the cross-corrugated elements.

The straight-channelled elements require adiabatic conditions and various geometries of these elements are possible. For example, straight channel monoliths are suitable for use in the process of the invention.

Cross-corrugated elements allow efficient heat transfer from the pipe wall to the gas stream. They are also suitable for use in the process of the invention.

Other catalysed structured elements can also be applied in the process of the invention. They can e.g. be catalyst pellets, catalyst attached to the tube wall or catalyst attached to structures attached to the tube wall.

Fig.1 shows a conventional system with a pre-reformer having a reheating section and a reformer.

5 Fig. 2 shows a system representing an embodiment of the process of the invention.

Fig. 1 depicts a conventional system where process gas of hydrocarbon feedstock [1] and steam [2] is introduced in a pre-reformer [20] at temperatures of about 450°C to 550°C.
10 By the steam reforming reactions proceeding in the pre-reformer, the temperature in the process gas usually decreases or increases slightly when carrying out the pre-reforming process depending on the hydrocarbon feedstock, feedstock as it is an adiabatic operation. The pre-reformed
15 product stream [4] and optionally carbon dioxide [8] enter the heating coil. The optional addition of CO₂ is indicated by a dashed line.

In industrial synthesis gas preparation plants, the pre-reformed process gas, to which CO₂ can be added, is subsequently reheated to the desired inlet temperature to the fired steam reformer [24] by heat exchange with hot flue gas [7] from the fired reformer [24]. The usual inlet temperature into an industrial reformer is between 500°C and
20 700°C.
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Fig. 2 illustrates an embodiment of the invention with two reheating sections and three sections with catalytic elements. In the process of the invention the amount of catalyst necessary for the process is completely decoupled from
30 the necessary heat transfer area.

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Hydrocarbon feed [1] is mixed with process steam [2] forming the feed stream [3] to the adiabatic pre-reformer [20]. This step is optional and can be left out if it is not required. CO₂ can then be added if desired to the pre-reformed product stream [4] or in the case where pre-reforming is not required, to the hydrocarbon and steam feed stream [3]. The mixture then enters a process heating coil [21] situated in the flue gas section [27] from a fired tubular reformer [29] utilising the heat content of the flue gas [12] to carry out steam reforming of the process stream. In heating coil [21], the pre-reformed stream [4] is heated to, for example, 600°C-700°C before being collected in a header system [22]. A structured element catalysed with steam reforming catalysts [22a] is situated inside header system [22]. Heated stream [4] passes through catalyst [22a] utilising the heat to steam reform the hydrocarbon content of the process stream and forming stream [5]. Steam [5] is led to a second process heating coil [23].

Stream [5] is heated to, for example, 600°C to 750°C in heating coil [23] before being collected in header system [24]. A structured element catalysed with steam reforming catalysts [24a] is situated inside header system [24] and heated stream [5] passes through catalyst [24a] utilising the heat to further steam reform the hydrocarbon content of the process stream forming stream [6]. Steam [6] is lead to a third process heating coil [25].

Stream [6] is heated to, for instance, 600°C to 800°C before being collected in header system [26]. A structured element catalysed with steam reforming catalysts [26a] is

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situated inside header system [26] and heated stream [6] passes through this catalyst utilising the heat to further steam reform the hydrocarbon content of the process stream forming stream [7].

5

Several more reheating and reaction steps can be included at this point. The number of reheating and reaction steps depends on the desired effect e.g. gas composition or equilibrium gas temperature.

10

If desired CO₂ can be added at each reaction step.

If no further reheating and reaction steps are required, steam [7] is led to the reforming tubes [28] situated in the fired tubular reformer [29]. Here additional heat is added to the process by firing fuel, and the desired reformed product [8] is collected from the reforming tubes.

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A suitable structured element used in the embodiment described above is the straight channel monolith.

20

The advantages of the apparatus and the process of the invention are several. The most important advantage is that the solid reforming catalyst can easily be replaced because it is present in easily accessible elements placed outside the waste heat section.

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EXAMPLES**Example 1**

5 A comparison of the amount of catalyst required in a process of the invention as compared to a conventional process was made.

10 The conventional process was carried out by feeding hydrocarbon and steam into a pre-reformer followed by heating in a coil in the flue gas-containing waste heat section of a tubular reformer. Initially the feed was heated prior to passage through the first adiabatic reactor containing steam reforming catalyst pellets. Subsequently the mixture was reheated and reacted again, the number of reheating and reaction steps repeated until four reheating steps and four
15 reaction steps altogether had been carried out.

20 In the a process of the invention a feed consisting of hydrocarbon and steam was fed into a pre-reformer followed by passage through a piping system in the flue gas-containing waste heat section of a tubular reformer. Initially the feed was heated prior to passage through the first adiabatic header system containing a catalysed structured element. Subsequently the mixture was reheated and reacted
25 again, the number of reheating and reaction steps repeated until four reheating steps and four reaction steps altogether had been carried out.

30 The initial inlet temperature to the first reheating coil after the pre-reformer was 450°C and the final outlet temperature was 650°C for both systems. Both systems were feed with a flow rate of 270 Nm³/h was led to the two steam re-

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forming systems, and the product was withdrawn at a rate of 319 Nm³/h. The carbon flow rate was 100 Nm³/h. The space velocity of the conventional process was 10.000 - 15.000 Nm³ C₁/hr m³ catalyst. In the process of the invention the
5 space velocity can be increased to 100.000 - 1.000.000 Nm³ C₁/hr m³ catalyst because the catalyst is supported on a structured element.

The catalyst amount used in the process of the invention
10 was 0.1-1.0 kg, while 6.7 to 10 kg were used in the conventional process.

The process of the invention allows the use of orders of magnitude less catalyst, allowing simplicity in design
15 leading to superior economics.

Example 2

This example is based on the systems described in Figures 1 and 2, without CO₂ addition. A waste heat boiler was placed
20 in the flue gas section of the reformer, required in order to obtain overall high energy efficiency by recovering the heat content in the flue gas.

The figures shown in Table 2 indicate that substantial savings are obtainable using the process of the invention.
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Table 2

Comparison of the duty distribution in
a Conventional process compared with
process of the invention

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	Conventional	Invention
Primary reformer duty, Gcal/h	40.3	22.6
Reheat coil duty, Gcal/h	5.3	n.a.
Reheat coil/header system with structure catalyst duty, Gcal/h	n.a.	12.0
Total Reforming Duty, Gcal/h	45.6	45.6
Flue Gas Flow, Nm ³ /h	105166	92054
Waste heat boiler duty, Gcal/h	9.8	2.0

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The results showed that the duty required by the reformer was much less in the case where the process of the invention was used. A smaller reformer can therefore be used in the process of the invention. The amount of steam generated was also reduced in addition to a flue gas flow rate reduction. Altogether substantial savings are achieved.

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CLAIMS

1. Process for the preparation of synthesis gas by catalytic steam and/or CO₂ reforming of a hydrocarbon feedstock
5 comprising the following steps:

- a. heating the reaction mixture of hydrocarbon feedstock and steam and/or CO₂ in the flue gas containing waste heat section from the fired tubular reformer
- b. adiabatic reforming of the reaction mixture outside the waste heat section by contact with a solid reforming catalyst
- c. repeating steps a. and b. until the desired reaction mixture composition and temperature is reached
- d. feeding the reaction mixture to the fired tubular reformer and further reforming the mixture to the desired composition and temperature,
15 wherein the adiabatic reforming of the reaction mixture is conducted in the process gas piping system in the flue gas-containing waste heat section, the piping system having adiabatic zones outside the heating section and containing solid reforming catalyst.

2. Process according to claim 1 wherein the reaction mixture of hydrocarbon and steam and/or CO₂ is pre-reformed
25 prior to heating step a.

3. Process according to claims 1 and 2 wherein the solid reforming catalyst is a catalysed structured element.

30 4. Process according to claim 3 wherein the structured element is cross-corrugated.

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5. Process according to claim 3 wherein the structured element is a monolith.

6. Process according to claim 3 wherein the structured element is a high surface structured element.

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7. Process according to claim 1 wherein the solid reforming catalyst is in adiabatic zones in the header system feeding and collecting process gas to- and from a heating coil.

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8. Process according to claim 1 wherein the solid reforming catalyst is in adiabatic zones of the coil tubes and/or in the tube-connecting elements.

15

9. Process according to claims 1-8 wherein the process gas piping system located inside the flue gas-containing waste heat section contains solid reforming catalyst.

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10. Apparatus for the preparation of synthesis gas according to claim 1 comprising the following:

a. an adiabatic pre-reformer for optional pre-reforming of a mixture of hydrocarbon feedstock and steam and/or CO₂

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b. a fired tubular reformer with a flue gas-containing waste heat section for heating of a mixture of hydrocarbon feedstock and steam and/or CO₂ or of the pre-reformed mixture

c. a process gas heating coil integrated in the flue gas-containing waste heat section

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d. a steam reforming unit system outside the waste heat section

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wherein the steam reforming unit system is integrated in the process gas piping system of the piping system of the heated coil system in the flue gas-containing waste heat section, the piping system having adiabatic zones outside the heating section and containing solid reforming catalyst.

11. Apparatus according to claim 10 wherein the solid reforming catalyst is in adiabatic zones in the header system feeding and collecting process gas to- and from the heating coil.

12. Apparatus according to claim 10 wherein the solid reforming catalyst is in the adiabatic zones of the coils and/or the tube-connecting elements.

13. Apparatus according to claim 10-12 wherein the process gas heating coil situated in the flue gas-containing waste heat section contain a solid reforming catalyst.

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ABSTRACT

Process and apparatus for the preparation of synthesis gas
by catalytic steam and/or CO₂ reforming of a hydrocarbon
5 feedstock comprising the following steps:

- a. heating the reaction mixture of hydrocarbon feed-
stock and steam and/or CO₂ in the flue gas containing
waste heat section from the fired tubular reformer
- 10 b. adiabatic reforming of the reaction mixture out-
side the waste heat section by contact with a solid
reforming catalyst
- c. repeating steps a. and b. until the desired reac-
tion mixture composition and temperature is reached
- 15 d. feeding the reaction mixture to the fired tubular
reformer and further reforming the mixture to the de-
sired composition and temperature,
wherein the adiabatic reforming of the reaction mix-
ture is conducted in the process gas piping system in
the flue gas-containing waste heat section, the piping
20 system having adiabatic zones outside the heating sec-
tion and containing solid reforming catalyst.

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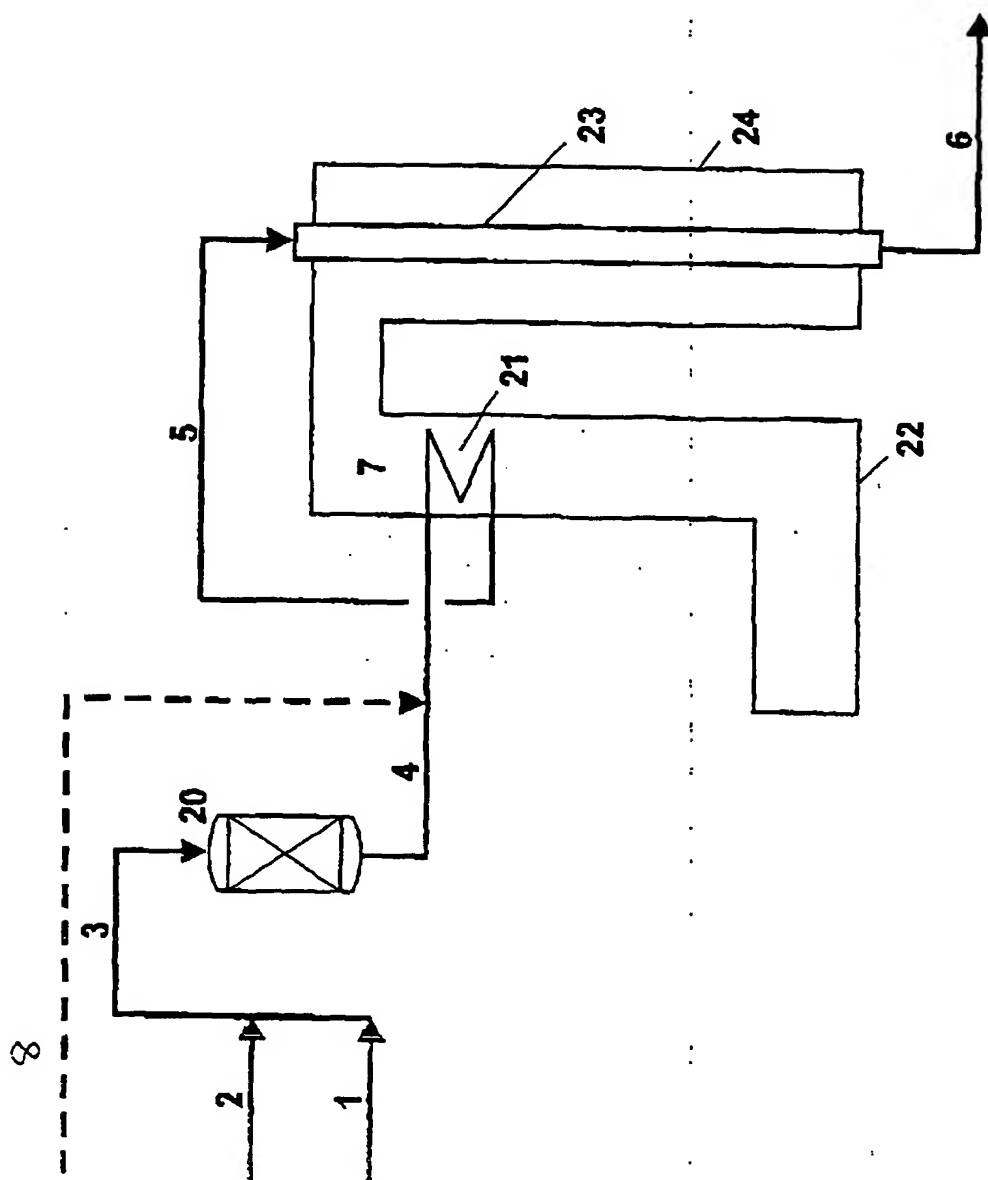


FIG. 1

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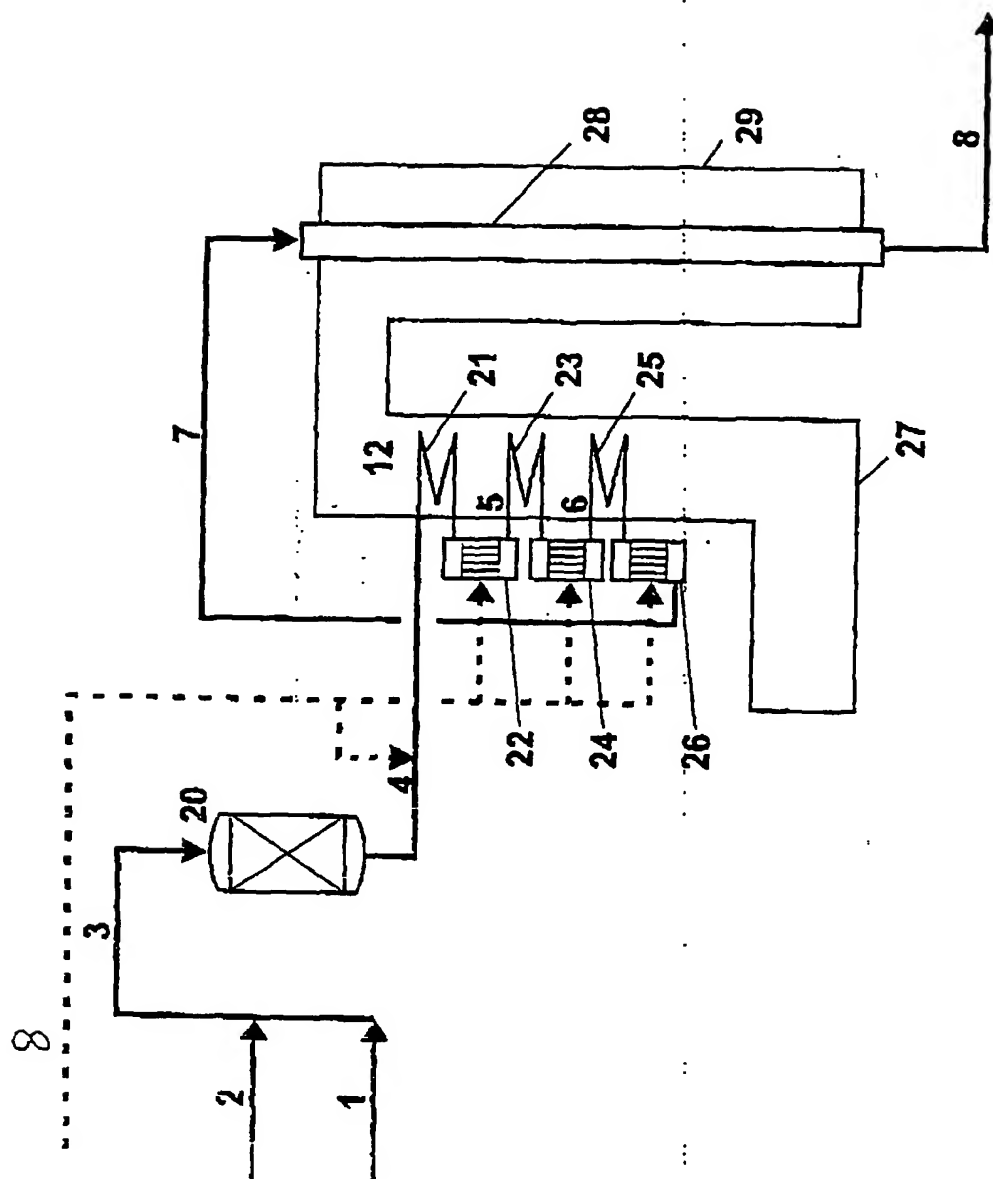


FIG. 2